

Tunable excitation source for coherent Raman spectroscopy based on a single fiber laser

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(Received 24 August 2011; accepted 12 October 2011; published online 1 November 2011)

We demonstrate a wavelength tunable optical excitation source for coherent Raman scattering (CRS) spectroscopy based on a single femtosecond fiber laser. Electrically controlled wavelength tuning of Stokes optical pulses was achieved with soliton self frequency shift in an optical fiber, and linear frequency chirping was applied to both the pump and the Stokes waves to significantly improve the spectral resolution. The coherent anti-Stokes Raman scattering (CARS) spectrum of cyclohexane was measured and vibrational resonant Raman peaks separated by 70 cm^{-1} were clearly resolved. Single laser-based tunable excitation may greatly simplify CRS measurements and extend the practicality of CRS microscopy. © 2011 American Institute of Physics.

[doi:10.1063/1.3657529]

Coherent Raman scattering (CRS) is a useful mechanism for spectroscopy and microscopy, with the ability to probe vibrational resonances of molecules and thus provide imaging contrast without fluorescence labeling.^{1,2} CRS effects are based on nonlinear mixing between pump, probe, and Stokes waves; the efficiency of CRS is proportional to the optical power density, and tight focusing intrinsically provides a sectioning function for microscopy.^{3,4} Biomedical spectroscopy and 3-dimensional imaging have been demonstrated with both coherent anti-Stokes Raman scattering (CARS)^{3,4} and stimulated Raman scattering (SRS).^{5,6} CARS originates from a four-wave mixing process between the pump at frequency ω_p and the Stokes at frequency ω_s , and the intensity of the anti-Stokes at $\omega_{as} = 2\omega_p - \omega_s$ is measured. The amplitude of the anti-Stokes beam is proportional to the 3rd order nonlinear susceptibility of the material, $\chi^{(3)}$. On the other hand, in SRS the high frequency pump transfers part of its energy into the lower frequency Stokes and thus introduces stimulated Raman gain (SRG) in the Stokes and stimulated Raman loss (SRL) in the pump.^{2,5} Practically, the laser excitation system is the most important part for CARS and SRS imaging as they both require short optical pulses for enhanced nonlinear response and a continuously tunable wavelength difference between the pump and the Stokes to probe the targeted Raman bands. In addition, the pulse repetition rate and the pulse arrival time between pump and Stokes have to be precisely synchronized to ensure effective nonlinear mixing between them.

A typical CRS system uses two feedback controlled Ti:Sapphire lasers or two optical parametric oscillators (OPOs) driven by the same pump to generate synchronized pump and Stokes pulses.³⁻⁷ Ti:Sapphire lasers are relatively bulky in size, and the tuning of their wavelengths through mechanical adjustments is generally slow and lacks repeatability. Recent advancements have made fiber-optic lasers highly reliable and relatively low-cost. A compact, turn-key

fiber laser-based excitation system would significantly simplify CRS microscopy and enable wider availability of CRS for various biological and biomedical applications. Unfortunately, continuous wavelength tuning of femtosecond fiber lasers over a wide window has not been achieved so far, and precise synchronization between two passively mode-locked fiber lasers also remains a challenging task. In addition, the optical power of a femtosecond fiber laser in the 800nm wavelength region is usually lower than that of a Ti:Sapphire laser, and therefore efficient utilization of pulse energy in the CRS process is critical.

In this letter, we demonstrate a CRS excitation source based on a single femtosecond fiber laser. Wavelength tuning between the pump and the Stokes was accomplished with soliton self-frequency shift (SSFS) in a photonic crystal fiber (PCF).^{8,9} Efficient wavelength shifting based on SSFS requires femtosecond optical pulses;^{10,11} however, the broad spectral linewidth of femtosecond pulses would result in poor spectral resolution for CRS which is not adequate for most biomedical applications. To circumvent this problem, we applied identical linear frequency chirp on the pump and Stokes pulses to significantly improve the spectral resolution. As an application example, the CARS spectrum of cyclohexane was measured with a spectral resolution of approximately 30 cm^{-1} using this single-laser-based excitation source.

The experimental setup is shown in Fig. 1. A fiber laser (IMRA Femtolite-100) generates 120 fs pulses at 806 nm with approximately 9 nm spectral linewidth, 100 mW average power and 75 MHz repetition rate, corresponding to a pulse energy of approximately 1.3 nJ. This laser output is split into the pump and the Stokes paths. The pump passes through a motorized delay stage (Opto-Sigma) and passes twice through a 5 cm-long glass rod (Schott SF-6) for pulse chirping. The Stokes path has a voltage-controlled variable optical attenuator (VOA) which controls the optical power that enters a 2 m-long PCF (Crystal Fiber NL-PM-750). By changing the applied voltage, the wavelength of the Stokes

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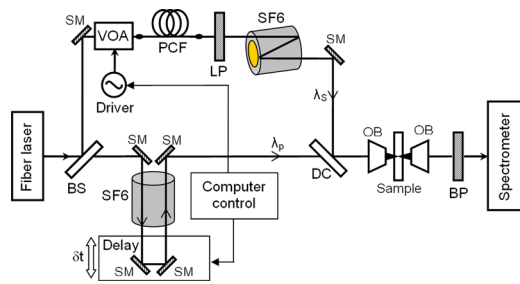


FIG. 1. (Color online) Experimental configuration with controllable Stokes wavelength (λ_s) and pump relative delay (δt). BS: beam splitter, SM: silver mirror, PCF: photonic crystal fiber, LP: long-pass filter, SF6: SF-6 glasses rod, DC: dichroic beam combiner, OB: objective lenses, and BP: band-pass filter.

could be varied from 850 nm to 1200 nm through SSFS.¹² The average optical power of the wavelength-shifted soliton at the PCF output is approximately 4 mW in the vicinity of 1000 nm, corresponding to a pulse energy of 53 pJ. In principle, the pulse-to-pulse wavelength stability of the soliton output can be affected by intensity noise and power fluctuations of the pump laser. Based on the power-wavelength characteristic of SSFS, a 0.1% RMS relative intensity noise of the fiber laser would produce on the order of 0.05 nm RMS wavelength error, which has negligible impact in the CARS measurement. A long-pass filter after the PCF blocks the residual power at 806 nm wavelength as well as the 2nd-order soliton generated below 850 nm. Another 5-cm SF6 glass rod in the Stokes path has end surfaces partially coated with gold so that the Stokes beam can fold back multiple times. The pump and the Stokes pulses are then combined with a 45° incidence dichroic filter and focused within the sample by a pair of objective lenses (Nikon 20x) in the confocal configuration. A bandpass filter rejects the pump and the Stokes components, and the anti-Stokes light is captured by a spectrometer (Ocean Optics). A laptop computer was used to control the Stokes wavelength through the VOA and the relative pulse delay between pump and Stokes via the motorized delay stage.

Liquid cyclohexane was used as the sample for the CARS measurement because of its well known Raman spectrum. In this measurement, we were particularly interested in the two closely spaced C-H stretches at wave numbers around 2923 cm⁻¹ and 2853 cm⁻¹. For transform-limited pump and Stokes pulses, the spectral resolution, $\Delta\nu_c$, of CARS is generally determined by $\delta\nu_c \approx \sqrt{1/(2\delta T_p)^2 + 1/(2\delta T_s)^2}/c$, where δT_p and δT_s are the

temporal widths of the pump and the Stokes pulses, and $c = 3 \times 10^{10}$ cm/s is the speed of light. With the 120-fs pump and Stokes optical pulses in our laser system, the spectral resolution would be approximately 200 cm⁻¹ which is not sufficient to resolve the two C-H stretches of cyclohexane separated by only 70 cm⁻¹.

One straightforward way to improve spectral resolution would be to use a narrowband optical filter to reduce the spectral linewidth of the excitation source.¹³ However, this would significantly reduce the pump and probe optical power and would not be acceptable for the fiber laser-based excitation system which is often limited by the available power. Another technique to improve the spectral resolution is to apply a linear chirp on the optical pulses.¹⁴⁻¹⁷ In previous work, due to the lack of an efficient wavelength tuning mechanism, broadband Stokes pulses were often used, either with ultra short optical pulses (<50 fs) or with supercontinuum generated in PCF. With linearly chirped optical pulses, a frequency scan of $\Delta\omega$ between the pump and the Stokes can be accomplished by a time scan of δt as illustrated in Fig. 2(a). Although the wide bandwidth, linearly chirped Stokes pulses may cover a large portion of the Raman spectrum for CARS spectroscopy,¹⁴⁻¹⁶ at any particular moment only a small fraction of the Stokes spectrum overlaps with the pump in the mixing process, while the Stokes power outside this time-overlapped region is wasted. By comparison, in our excitation system the temporal and spectral widths of the pump and the Stokes are similar, as illustrated in Fig. 2(b). This ensures the maximum level of overlap between the pump and the Stokes pulses in the nonlinear mixing process, and thus maximizes the power efficiency.

In our experiment, SF6 glass rods were used to introduce pulse chirping. As the chromatic dispersion of the glass is higher for the pump at 806 nm than for the Stokes at around 1000 nm, the pump passes through the 5-cm glass rod twice, while the Stokes has to pass through the rod 3 times in the fold-back configuration. As a result, both the pump and the Stokes pulses were stretched to approximately 700 fs, improving the spectral resolution to approximately 30 cm⁻¹. Fig. 3(a) is a (color online) plot which shows the spectrum of measured anti-Stokes light originated from CARS as a function of the linearly scanned Stokes wavelength. The two C-H stretches of cyclohexane separated by 70 cm⁻¹ are clearly separated with the help of linear pulse chirping. It is interesting to note that, in this measurement, the resolution of CARS spectroscopy is not determined by the spectral width of the

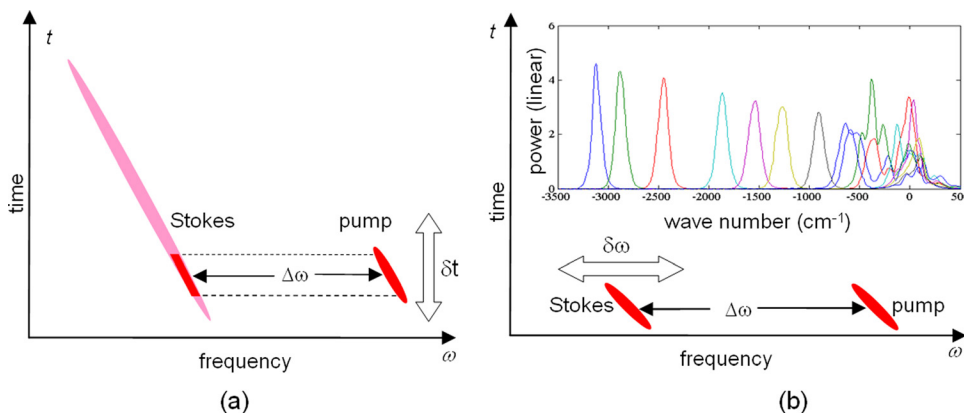


FIG. 2. (Color online) Illustration of linear frequency chirp for coherent Raman spectroscopy (a) with wideband but fixed-wavelength Stokes and (b) with wavelength tunable Stokes. Inset: soliton self frequency shift introduced with power control.

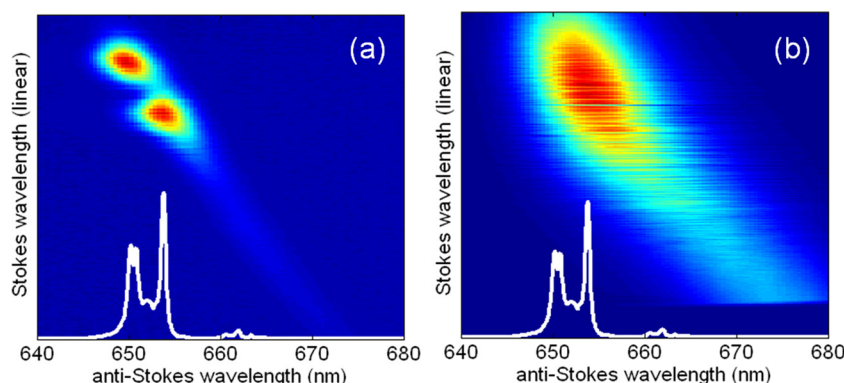


FIG. 3. (Color online) Color plots of measured anti-Stokes intensity of cyclohexane as a function of anti-Stokes wavelength and the linear scan of the Stokes wavelength (a) with linear chirp to both pump and Stokes pulses and (b) without linear chirp applied. The white line in the figure indicates the spontaneous Raman spectrum.

anti-Stokes signal; rather, it is determined by the temporal width of the chirped pulses and the parallelism between the pump and the Stokes pulses in the frequency-time diagram as illustrated in Fig. 2. As a comparison, Fig. 3(b) shows the same measurement but with both SF6 glass rods removed. As expected, without linear chirping, the spectral resolution is poor and it is not possible to resolve the two closely spaced vibrational resonant Raman peaks (indicated by the white curve shown in the same figure).

One practical issue in the CRS excitation source based on SSFS is the dependence of Stokes pulse propagation delay as a function of its central wavelength, which creates differential pulse walk-off between the pump and Stokes pulses during wavelength tuning. To obtain the results shown in Fig. 3, we had to adjust the delay line to optimize the temporal delay between the pump and the Stokes pulses when the Stokes wavelength was tuned. Since the wavelength-dependent propagation delay of the Stokes is determined by the chromatic dispersion parameter of the PCF, which is deterministic, the computer-controlled delay stage in the measurement setup could effectively compensate for this differential pulse walk off.

In conclusion, we have demonstrated a wavelength tunable and power-efficient optical excitation source for coherent Raman scattering measurements. Electrically controlled wavelength tuning of femtosecond optical pulses was achieved with soliton self frequency shift, and a spectral resolution of 30 cm^{-1} was obtained with linear frequency chirping of both the pump and the Stokes waves. The CARS spectrum of cyclohexane was measured, and the vibrational resonant Raman peaks separated by 70 cm^{-1} were clearly resolved. Although we have only provided an application example of CARS, the technique can also be used for other

CRS applications such as SRS. This tunable CRS excitation source based on a single fiber laser greatly simplifies the CRS imaging system in order to make CARS and SRS more practical and easy to use.

This work was supported by the National Institute of Health under Grant No. NIH-RR023142 and NIH-1R21RR032377.

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